



weight, and preferably lower than 15% in weight and more preferably in the order of 10 % in weight based on the total volume of the composition.

3. A composition according to claim 1 or 2, characterized in that the polyethylene glycol a) comprises 75 to 600 ethylene oxide groups per molecule.

4. A composition according to claim 3, characterized in that the polyethylene glycol is selected amongst the polyethylene glycols PEG-90, PEG-100, PEG-135, PEG-180, PEG-200, PEG-240, PEG-350 and PEG-454.

5. A composition according to claim 1 or 2, characterized in that, in the case of a block polymer with ethylene oxide and propylene oxide blocks b), having the formula 2), at least one of x and z is equal to or higher than 80 and y is higher than 45.

6. A composition according to claim 5, characterized in that x and z are equal to 98 and y is equal to 67.

7. A composition according to any of the preceding claims, characterized in that the physiologically acceptable medium is a solubilizing medium for the oxyethylenated polymer, preferably having a bacteriological property.

8. A composition according to any of the preceding claims, characterized in that the physiologically acceptable medium comprises a solvent or a mixture of solvents for the oxyethylenated polymer.

9. A composition according to claim 8, characterized in that the solvent is selected amongst water, alcohols, ethers, dimethylsulfoxide, N-methylpyrrolidone, acetones, and the mixtures thereof.

10. A composition according to claim 9, characterized in that the alcohols are selected amongst alkanols, benzyl alcohol or alkanediols.

11. A composition according to claim 10, characterized in that the alkanols are (C<sub>1</sub>-C<sub>6</sub>) lower alkanols, preferably ethanol and isopropanol.

12. A composition according to claim 10, characterized in that the alkanediols are selected amongst ethylene glycol, propylene glycol and pentanediol.

13. A composition according to claim 9, characterized in that the solvent is a water/alcohol mixture.

14. A composition according to claim 13, characterized in that the alcohol accounts up to 80 % in volume of the water/alcohol mixture.

15. A composition according to claim 14, characterized in that the water/alcohol mixture is a water/ethanol mixture comprising 70% in volume of ethanol based on the weight of the water/ethanol mixture.

16. A composition according to any of the preceding claims, characterized in that it additionally contains cosmetic builders selected amongst conventional gellants and/or thickening agents, anionic, non ionic, cationic or amphoteric surfactants, propenetrating agents, emulsifiers, perfumes, preservatives, fillers, sunscreens, proteins, vitamins, provitamins, anionic, non ionic, cationic or amphoteric non fixing polymers, hydrating agents, emollients, softening agents, mineral, vegetable or synthetic oils, hydrophilic or lipophilic active ingredients such as ceramides and pseudoceramides, anti-foaming agents, antiperspirant agents, anti-free radical agents, bactericides, sequestrants, anti-dandruff agents, alkalinizing agents, volatile or non volatile, linear or cyclic, modified or not, silicones, polyols, and any other additive conventionally used in cosmetic compositions intended to be applied on the hair.

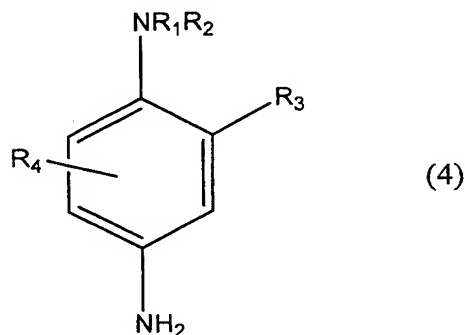
17. A method for limiting the penetration into the skin and/or the keratin fibres of at least one dye, preferably one oxydation dye, contained in a hair dyeing composition, characterised in that it comprises applying on the hair scalp and on the hair, as a pre-treatment, before a hair dyeing process using the hair dyeing composition, a hair pre-treatment anti-penetration compositions such as defined according to any of claims 1 to 16.

18. A method according to claim 17, characterized in that the application duration on the hair scalp and on the hair of the antipenetrating composition is from 5 seconds to one hour, and preferably from 1 to 10 minutes.

19. A method according to claim 17 or 18, characterized in that oxidation dye is selected amongst oxidation bases, coupling agents, orthodiphenols and the mixtures thereof.

20. A method according to claim 19, characterized in that the oxidation bases are selected amongst ortho- and para-phenylene diamines,

21. A method according to claim 20, characterized in that the oxidation bases are selected amongst para-phenylenediamines having the formula (4):



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where:

$R_1$  represents a hydrogen atom, a  $C_1-C_4$  alkyl moiety, a  $C_1-C_4$  monohydroxyalkyle,  $C_2-C_4$  polyhydroxyalkyl,  $(C_1-C_4)$ alkoxy( $C_1-C_4$ )alkyl,  $C_1-C_4$  alkyl substituted by a nitrogen, phenyl or 4'-aminophenyl group;

10  $R_2$  represents a hydrogen atom,  $C_1-C_4$  alkyl radical, a  $C_1-C_4$  monohydroxyalkyl or  $C_2-C_4$  polyhydroxyalkyle,  $(C_1-C_4)$ alkoxy( $C_1-C_4$ )alkyl or  $C_1-C_4$  alkyl substituted by a nitrogen group;

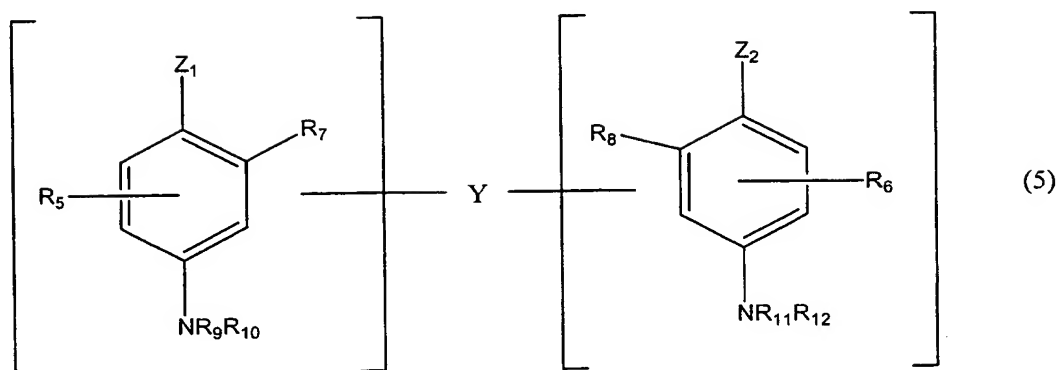
$R_3$  represents a hydrogen atom, a halogen atom such as a chlorine atom, a  $C_1-C_4$  alkyl moiety, a sulfo, carboxy, a  $C_1-C_4$  monohydroxyalkyle  
15 or  $C_1-C_4$  hydroxyalkoxy,  $C_1-C_4$  acetylaminoalkoxy,  $C_1-C_4$  mesylaminoalkoxy or  $C_1-C_4$  carbamoylaminoalkoxy;

$R_4$  represents a hydrogen, halogen atom or a  $C_1-C_4$  alkyl moiety;

$R_1$  and  $R_2$  may also form with the nitrogen atom carrying them a 5 or 6 members nitrogen heteroring optionally substituted by one or more  
20 alkyl, hydroxy or ureido groups.

22. A method according to claim 21, characterized in that the para-phenylenediamines are selected amongst paraphenylenediamine, paratoluylenediamine, 2-isopropyl-paraphenylenediamine, 2- $\beta$ -hydroxyethyl-paraphenylenediamine, 2,6-dimethyl-paraphenylenediamine,  
25 N,N-bis-( $\beta$ -hydroxyethyl)-paraphenylenediamine, 2-chloro-paraphenylenediamine, and their addition salts with an acid.

23. A method according to claim 20, characterized in that the oxidation bases are double bases having the formula (5):

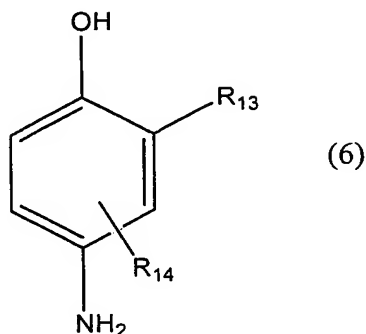


where:

- $\text{Z}_1$  and  $\text{Z}_2$ , whether identical or different, represent a hydroxyl or  $-\text{NH}_2$  moiety optionally substituted by a  $\text{C}_1\text{-C}_4$  alkyl moiety or by a Y-binding-branch;
- the Y binding branch represents an alkylene chain comprising 1 to 14 carbon atoms, linear or branched, able to be interrupted or ending with one or more nitrogen groups and/or by one or more heteroatoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted by one or more  $\text{C}_1\text{-C}_6$  hydroxyl or alkoxy moieties;
- $\text{R}_5$  and  $\text{R}_6$  represent a hydrogen or a halogen atom, a  $\text{C}_1\text{-C}_4$  alkyl,  $\text{C}_1\text{-C}_4$  monohydroxyalkyl,  $\text{C}_2\text{-C}_4$  polyhydroxyalkyl,  $\text{C}_1\text{-C}_4$  aminoalkyl moiety or a Y binding branch;
- $\text{R}_7$ ,  $\text{R}_8$ ,  $\text{R}_9$ ,  $\text{R}_{10}$ ,  $\text{R}_{11}$  and  $\text{R}_{12}$ , whether identical or different, represent a hydrogen atom, a Y binding branch or a  $\text{C}_1\text{-C}_4$  alkyl moiety; on the condition that the compounds with formula (5) only have one Y binding branch per molecule.

24. A method according to claim 23, characterized in that the double bases are selected amongst N,N'-bis-( $\beta$ -hydroxyethyl) N,N'-bis-(4'-aminophenyl) 1,3-diamino propanol, N,N'-bis-( $\beta$ -hydroxyethyl) N,N'-bis-(4'-aminophenyl) ethylenediamine, N,N'-bis-(4-aminophenyl) tetramethylenediamine, N,N'-bis-( $\beta$ -hydroxyethyl) N,N'-bis-(4-aminophenyl) tetramethylenediamine, N,N'-bis-(4-methyl-aminophenyl) tetramethylenediamine, N,N'-bis-(ethyl) N,N'-bis-(4'-amino, 3'-methyl) ethylenediamine, 1,8-bis-(2,5-diaminophenoxy)-3,5-dioxaoctane, and their addition salts with an acid.

25. A method according to claim 20, characterized in that the oxidation bases are para-aminophenols having the formula (6):



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where:

- $R_{13}$  represents a hydrogen atom, a halogen atom such as fluorine, a  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  monohydroxyalkyl,  $(C_1$ - $C_4$ ) alkoxy( $C_1$ - $C_4$ ) alkyl, or  $C_1$ - $C_4$  aminoalkyl, or  $C_1$ - $C_4$  hydroxyalkyl aminoalkyl ( $C_1$ - $C_4$ ) moiety; and
- $R_{14}$  represents a hydrogen atom or a halogen atom such as fluorine, a  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  monohydroxyalkyle,  $C_2$ - $C_4$  polyhydroxyalkyle,  $C_1$ - $C_4$  aminoalkyl,  $C_1$ - $C_4$  cyanoalkyl or  $(C_1$ - $C_4$ )alkoxy( $C_1$ - $C_4$ )alkyl moiety.

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26. A method according to claim 25, characterized in that the para-aminophenols are selected amongst para-aminophenol, 4-amino-3-methyl-phenol, 4-amino-3-fluoro-phenol, 4-amino-3-hydroxymethyl-phenol, 4-amino-2-methyl-phenol, 4-amino-2-hydroxymethyl-phenol, 4-amino-2-methoxymethyl-phenol, 4-amino-2-aminomethyl-phenol, 4-amino-2-( $\beta$ -hydroxyethyl-aminomethyl)-phenol, and their addition salts with an acid.

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27. A method according to claim 20, characterized in that the oxidation bases are orthodiphenols selected amongst 2-amino-phenol, 2-amino-1-hydroxy-5-methyl-benzene, 2-amino-1-hydroxy-6-methyl-benzene, 5-acetamido-2-amino-phenol, and their addition salts thereof with an acid.

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28. A method according to claim 20, characterized in that the oxidation bases are heterocyclic bases selected amongst pyridine derivates,

pyrimidine derivates, pyrazoline derivates, and their addition salts with an acid.

29. A method according to claim 28, characterized in that the pyridine derivates are selected amongst 2,5-diamino-pyridine, 2-(4-methoxyphenyl)amino-3-amino-pyridine, 2,3-diamino-6-methoxy-pyridine, 2-( $\beta$ -methoxyethyl)amino-3-amino-6-methoxy pyridine, and 3,4-diamino-pyridine.

30. A method according to claim 28, characterized in that the pyrimidine derivates are selected amongst 2,4,5,6-tetra-aminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2,5,6-triaminopyrimidine, and the pyrazolo-pyrimidine derivates such as those mentioned in Patent Application FR-A-2 750 048 and amongst which one can mention pyrazolo-[1,5-a]-pyrimidine-3,7-diamine; 2,5-dimethyl-pyrazolo-[1,5-a]-pyrimidine-3,7-diamine; pyrazolo-[1,5-a]-pyrimidine-3,5-diamine; 2,7-dimethyl-pyrazolo-[1,5-a]-pyrimidine-3,5-diamine; 3-amino-pyrazolo-[1,5-a]-pyrimidin-7-ol; 3-amino-pyrazolo-[1,5-a]-pyrimidin-5-ol; 2-(3-amino pyrazolo-[1,5-a]-pyrimidin-7-ylamino)-ethanol; 2-(7-amino-pyrazolo-[1,5-a]-pyrimidin-3-ylamino)-ethanol; 2-[(3-amino-pyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxy-ethyl)-amino]-ethanol; 2-[(7-amino-pyrazolo-[1,5-a]pyrimidin-3-yl)-(2-hydroxy-ethyl)-amino]-ethanol; 5,6-dimethyl-pyrazolo-[1,5-a]-pyrimidine-3,7-diamine; 2,6-dimethyl-pyrazolo-[1,5-a]-pyrimidine-3,7-diamine; 2,5,N7,N7-tetramethyl-pyrazolo-[1,5-a]-pyrimidine-3,7-diamine; 3-amino-5-methyl-7-imidazolylpropylamino pyrazolo-[1,5-a]-pyrimidine; and the addition salts thereof and their tautomeric forms, when there is a tautomeric balance.

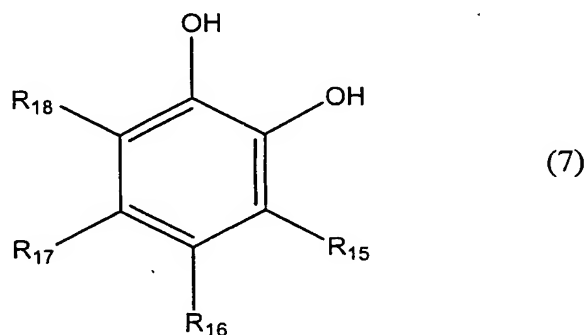
31. A method according to claim 28, characterized in that the pyrazole derivates are selected amongst 4,5-diamino-1-methyl-pyrazole, 3,4-diamino-pyrazole, 4,5-diamino-1-(4'-chlorobenzyl)-pyrazole, 4,5-diamino 1,3-dimethyl-pyrazole, 4,5-diamino-3-methyl-1-phenyl pyrazole, 4,5-diamino 1-methyl-3-phenyl-pyrazole, 4-amino-1,3-dimethyl-5-hydrazino-pyrazole, 1-benzyl-4,5-diamino-3-methyl-pyrazole, 4,5-diamino-3-tert-butyl-1-methyl pyrazole, 4,5-diamino-1-tert-butyl-3-methyl-pyrazole, 4,5-diamino-1-( $\beta$ -hydroxyethyl)-3-methyl pyrazole, 4,5-diamino-1-( $\beta$ -hydroxyethyl)- pyrazole, 4,5-diamino-1-ethyl-3-methyl-pyrazole, 4,5-

diamino-1-ethyl-3-(4'-methoxyphenyl)-pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethyl-pyrazole, 4,5-diamino-3-hydroxymethyl-1-methyl-pyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropyl-pyrazole, 4,5-diamino-3-methyl-1-isopropyl-pyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethyl-pyrazole, 4,5-triamino-pyrazole, 1-methyl-3,4,5-triamino-pyrazole, 3,5-diamino-1-methyl-4-methylamino-pyrazole, and 3,5-diamino-4-( $\beta$ -hydroxyethyl)amino-1-methyl-pyrazole.

32. A method according to any of claims 20 to 31, characterized in that the oxidation base accounts for 0.0005 to 12 % in weight, more preferably from 0.005 to 8 % in weight of the total weight of the composition.

33. A method according to claim 19, characterized in that the orthodiphenols comprise a condensed benzene ring or an aromatic ring carrying at least two hydroxyl groups on two consecutive carbon atoms of the ring.

34. A method according to claim 33, characterized in that the orthodiphenols are compounds having the formula:



where the  $R_{15}$  to  $R_{18}$  substituents, identical or different, represent a hydrogen atom, a halogen, hydroxyl, carboxyl, alkyl carboxylate, optionally substituted amino moiety, optionally substituted linear or branched alkyl, optionally substituted linear or branched alkenyl, optionally substituted cycloalkyl, alkoxy, alkoxyalkyl, alkoxyaryl, the aryl group being optionally substituted, aryl, aryl substituted, an optionally substituted heterocyclic moiety, a moiety optionally containing one or more silicon atoms, where two of the  $R_{15}$  to  $R_{18}$  substituents form together a saturated or an unsaturated ring optionally containing one or more heteroatoms and



optionally condensed with one or more saturated or unsaturated rings optionally containing one or more heteroatoms.

35. A method according to claim 33, characterized in that the orthodiphenols are selected amongst flavanols, flavonols, anthocyaninidins, anthocyanines, hydroxybenzoates, flavones, iridoids, such compounds  
5 being optionally osylated and/or in the form of oligomers, optionally osylated hydroxystilbenes, 3,4-dihydroxyphenylalanine and the derivatives thereof, 2,3-dihydroxyphenylalanine and the derivatives thereof, 4,5-dihydroxyphenylalanine and the derivatives thereof, 4,5-dihydroxyindole and  
10 the derivatives thereof, 5,6-dihydroxyindole and the derivatives thereof, 6,7-dihydroxyindole and the derivatives thereof, 2,3-dihydroxyindole and the derivatives thereof, dihydroxycinnamates, hydroxycoumarins, hydroxyisocoumarins, hydroxycoumarones, hydroxyisocoumarones, hydroxychalcones, hydroxychromones, anthocyanes, quinones,  
15 hydroxyxantones, and the mixtures of two or more of the previous compounds.

36. A method according to claim 35, characterized in that the orthodiphenols are selected amongst 5,6-dihydroxyindole and 5,6 dihydroxyindole carboxylic acid.

20 37. A method according to one of claims 19 to 36, characterized in that the orthodiphenols are contained in plant, fruit or citrus fruit extracts as well as in mixtures of such extracts.

38. A method according to claim 37, characterized in that the orthodiphenols are contained in tea, grape, apple, banana, or potato extracts,  
25 as well as in mixtures of such extracts.

39. A method according to claim 19 characterized in that the coupling agents are selected amongst meta-aminophenols, meta-phenylenediamines, metadiphenols, naphthols and heterocyclic coupling agents such as for example, indole derivatives, indolin derivatives, sesamol and  
30 the derivatives thereof, pyridine derivatives, pyrazolotriazole derivatives, pyrazolones, indazoles, benzimidazoles, benzothiazoles, benzoxazoles, 1,3-benzodioxoles, quinolins and their addition salts with an acid.

40. A method according to claim 39, characterized in that the coupling agents are selected amongst 2,4-diamino 1-( $\beta$ -hydroxyethyloxy)  
35 benzene, 2-methyl 5-amino phenol, 5-N-( $\beta$ -hydroxyethyl)amino 2-methyl

phenol, 3-amino phenol, 1,3-dihydroxy benzene, 1,3-dihydroxy 2-methyl benzene, 4-chloro 1,3-dihydroxy benzene, 2-amino 4-( $\beta$ -hydroxyethylamino) 1-methoxy benzene, 1,3-diamino benzene, 1,3-bis-(2,4-diaminophenoxy) propane, sesamol, 1-amino 2-methoxy 4,5-methylenedioxy benzene,  $\alpha$ -naphthol, 6-hydroxy indole, 4-hydroxy indole, 4-hydroxy N-methyl indole, 6-hydroxy indoline, 2,6-dihydroxy 4-methyl pyridine, 1-H 3-methyl pyrazole 5-one, 1-phenyl 3-methyl pyrazole 5-one, 2-amino 3-hydroxypyridine, 3,6-dimethyl-pyrazolo-[3,2-c]-1,2,4-triazole, 2,6-dimethyl-pyrazolo-[1,5-b]-1,2,4-triazole and the addition salts thereof  
 10 with an acid.

41. A method according to claim 39 or 40, characterized in that coupling agent(s) account(s) for 0.0001 to 15% in weight of the total weight of the composition, and preferably from 0.001 to 10%.

42. A method according to one of claims 17 to 41, characterized in  
 15 that the hair dyeing composition comprise one or more direct dyes, preferably selected from the nitrated, azoic or anthraquinonic, neutral, cationic or anionic dyes.

43. A method according to claim 42 characterized in that direct dyes account for 0.001 to 20% in weight, preferably from 0.01 to 10% in  
 20 weight of the total weight of the composition.

44. A method according to any of claims 17 to 43, characterized in that the hair dyeing composition comprises one or more amino acids and/or one or more proteins.

45. A method according to claim 44, characterized in that the amino  
 25 acids comprise at least one thiol group and are selected amongst amino acids having an amine function in position  $\alpha$  compared with a carboxylic acid function.

46. A method according to claim 45, characterized in that amino acid(s) is/are selected amongst cystein and the derivates thereof, the  
 30 proteins are selected amongst glutathione and the derivates thereof.

47. A method according to one of claims 42 to 46, characterized in that the molar ratio of the amino acid(s) and of the protein(s) to the other oxidation dyes varies from 0.001 to 50, preferably from 0.01 to 5, and more preferably from 0.05 to 2.5.

48. A method according to any of claims 17 to 47, characterized in that the hair dyeing composition further comprises an enzyme.

49. A method according to claim 48, characterized in that the enzyme is selected amongst pyranose oxydases glucose oxydases, glycerol  
5 oxydases, lactate oxidases, pyruvate oxidases, uricases, cholin oxidases, sarcosin oxidases, bilirubin oxydases, laccases, tyrosinases, peroxidases, catalases, superoxydesdimutases and the mixtures thereof, or amongst plant or animal extracts containing the above-mentioned enzymes.

50. A method according to claim 49, characterized in that the  
10 enzyme is selected amongst the tyrosinases.

51. A method according to claim 49 or 50, characterized in that the hair dyeing composition comprises  $5 \cdot 10^{-3}$  to 5 mg, preferably  $5 \cdot 10^{-2}$  to 0,5 mg of enzyme per millilitre of final composition.

52. A method according to any of claims 17 to 51, characterized in  
15 that the oxidation dye is present in an amount ranging from 1 mM to 10 mM per litre of composition.

53. A method according to any of claims 17 to 52, characterized in that the hair dyeing composition further comprises an effective amount of a system comprising a first component selected amongst the Mn(II) and/or  
20 Zn(II) salts and oxide and the mixtures thereof and a second component selected amongst alkaline hydrogenocarbonates, earth alkaline hydrogenocarbonates and the mixtures thereof, the proportions of the first and second component are such that:

25 
$$\frac{[Mn(II)]}{[HCO_3]} \leq 1 \text{ with } [Mn(II)] \neq 0$$

$$\frac{[Zn(II)]}{[HCO_3]} \leq 1 \text{ with } [Zn(II)] \neq 0$$

$$\frac{[Mn(II) + Zn(II)]}{[HCO_3]} \leq 1 \text{ with } [Mn(II)] \text{ and } [Zn(II)] \neq 0$$

30

where [Mn(II)], [Zn(II)] and [HCO<sub>3</sub>] represent respectively the Mn(II), Zn(II) molar concentrations and HCO<sub>3</sub> in the composition.

54. A composition according to claim 53, characterized in that the ratio  $\frac{[Mn(II)]}{[HCO_3]}$  varies from  $10^{-5}$  to  $10^{-1}$ , preferably from  $10^{-3}$  to  $10^{-2}$ , and more preferably is in the order of  $5 \cdot 10^{-3}$ .

55. A composition according to claim 53 or 54, characterized in that the ratio  $\frac{[Zn(II)]}{[HCO_3]}$  varies from  $10^{-4}$  to 1, preferably from  $10^{-3}$  to 1, and more preferably is in the order of  $5 \cdot 10^{-1}$ .

56. A composition according to any of claims 53 to 55, characterized in that the ratio  $\frac{[Mn(II) + Zn(II)]}{[HCO_3]}$  varies from  $10^{-5}$  to  $10^{-1}$ , preferably  $10^{-3}$  to  $10^{-2}$ .

10 57. A composition according to any of claims 53 to 55, characterized in that the Mn(II) and Zn(II) salts are selected amongst chloride, fluoride, iodure, sulphate, phosphate, nitrate, perchlorate, and carboxylic acid salts and the mixtures thereof.

58. A composition according to any of claims 53 to 57, characterized in that the Mn(II) and/or Zn(II) salt is a chloride.

59. A composition according to any of claims 53 to 58, characterized in that the carboxylic acid salts are hydroxylated carboxylic acid salts.

60. A composition according to any of claims 53 to 58, characterized in that the hydroxylated carboxylic acid salt is gluconate.

61. A composition according to any of claims 53 to 60, characterized in that the hydrogenocarbonate is selected amongst sodium hydrogenocarbonate, potassium hydrogenocarbonate and the mixtures thereof.